AD-A032 414   PRINCETON UNIV   N J SOLID STATE AND MATERIALS LAB   F/G 7/4
              THE STABILITY, ELECTRONIC AND SURFACE PROPERTIES OF THE ALKALI --ETC(U)
              SEP 76   B S ROYCE   DAAG29-73-C-0019
UNCLASSIFIED   PSSL-010976   ARO-11330.6-C   NL

I OF I
AD·A
032 414

E N D
DATE
FILMED
1-21-77
NTIS

THE STABILITY, ELECTRONIC AND SURFACE
PROPERTIES OF THE ALKALI AZIDES

PRINCETON UNIVERSITY, NEW JERSEY

1 SEPTEMBER 1976

334106

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

 ORO-11330.6-C

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER PSSL 010976	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* The Stability, Electronic and Surface Properties of the Alkali Azides		5. TYPE OF REPORT & PERIOD COVERED Final 1 April 1973 30 June 1976
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Barrie S. H. Royce		8. CONTRACT OR GRANT NUMBER(s) DAAG29-73-C-0019
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Laboratory Princeton University Princeton, N. J. 08540		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 1 September 1976
		13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

D D C

NOV 15 1976

B

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

NA

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Alkali Azides, Thermal Decomposition, KN_3, Born Calculations Azide Potential, Field Effects

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Measurements of the thermal decomposition of KN_3 are reported. The decomposition was found to be enhanced by the application of an electric field with the increased rate of nitrogen evolution due to the field being essentialy independent of the sign of the field whereas the potassium evolution rate was found to be largest when the free surface of the crystal was negative. A model for this behavior is proposed.

DD `FORM 1 JAN 73` 1473 EDITION OF

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

AD A032414

#20 cont'ed.

Theoretical calculations of the energies of Schottky pair formation, cation ion migration, cohesive energies, lattice parameters, specific volumes, azide liberational frequencies and elastic moduli are also outlined. These have been made using a Born model of the azide lattice and attention directed at chosing a correct form for the azide repulsive potential. A bispherical form for this potential was developed and found to be superior in predicting the above properties over the series of alkali azides. Using the energies obtained in the above calculations an analysis of cation diffusion in KN_3 has been carried out. An approximate analytic expression for the correlation factor was obtained and the temperature dependence of the elements of the diffusion temperature evaluated.

ACCESSION for

NTIS   White Section
DDC   Buff Section
UNANNOUNCED
JUSTIFICATION

BY
DISTRIBUTION/AVAILABILITY CODES

Dist.   AVAIL. and/or SPECIAL

A

The Stability, Electronic and Surface Properties
of the Alkali Azides

Introduction

The cause of metastability in solid materials is of interest from both the technological and scientific viewpoint. The azides have been extensively studied [1] since the heavy metal azides are important primary explosives whereas the alkali azides exhibit controlled decomposition behavior. This last feature enables measurements to be made in a convenient time frame and the effects of various stimuli on the slow decomposition reactions to be examined. Thermal, optical and electronic stimuli can all initiate both the violent and controlled decomposition reactions and for each of these initiation processes the problem is to decide how the available energy is localized in the lattice to give the final products of decomposition. For KN_3, which has been the major material examined in the experimental part of the research reported below, the decomposition products are the alkali metal and nitrogen gas with the overall reaction following the form: $2KN_3 \to 3N_2 + 2K$. Of particular interest from the solid state reaction point of view are the rate limiting processes controlling the decomposition reaction which involves an electron transfer mechanism between the azide and metal ion with the subsequent interaction of two azide molecules to give rise to the three molecules of nitrogen gas. The reaction as usually represented is felt to follow the sequence given below:

$$N_3^- \xrightarrow{\text{Excitation}} N_3^{-*} \longrightarrow N_3^0 + e^- \tag{1}$$

$$M^+ + e^- \to M^\circ$$

$$2N_3^0 \to 3N_2$$
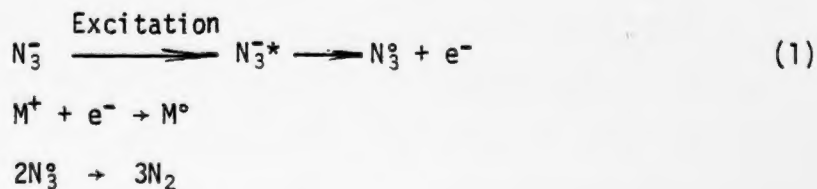
The removal of the electron from the azide ion via its prior elevation to an excited state is often considered to be the rate limiting process in thermal decomposition. Electric field experiments on AgN_3 by Zakhavov et al [2] have lead these workers to suggest that the final reaction above may be rate limiting, the azide molecules behaving as positive holes in the lattice and their lifetime being governed by the density of electrons.

The experiments outlined briefly below were designed to obtain data under controlled conditions so that the sequence of reactions represented in (1) could be examined to determine their relative importance as the rate controlling step in decomposition.

The alkali azides are ionic materials and it is therefore possible to apply a modified Born model [3] to the calculation of the cohesive properties of the azides. The major problem in applying this well established technique to the alkali azides is the development of a proper form of the azide ion repulsive potential. Three forms of this potential were examined and applied to the study of the cohesive energies, lattice parameters, specific volumes, azide liberational frequencies and elastic moduli in the alkali azides. The form of the azide repulsive potential was established by fitting to experimental data on KN_3 and the same parameters were used to evaluate the properties of the other alkali azides. A theoretical analysis of cation diffusion in KN_3 was carried out using the same forms of the lattice potential and migration energies determined in the prior calculations.

Experimental

a) <u>Crystal Growth</u> (with A. de Panafieu and A. Mandelis)

Potassium azide decomposes thermally in the solid state but the decomposition rate is low enough that a melt of the azide can be maintained.

The liquid is itself decomposing and strict temperature control is needed to prevent uncontrolled decomposition from occurring. The viscosity of the melt in the narrow temperature window below the onset of this uncontrolled decomposition is low enough that the evolved nitrogen gas can escape from the melt. As was first demonstrated by Appelton and Sharma [4] it is possible to use the Kyropolus technique for growing single crystals of KN_3 from the melt. The apparatus used and the method followed was essentially the same as that used by these authors. Single crystals of good transparency, exhibiting the expected symmetry were grown in a series of runs. There, together with samples supplied by Sharma and other Kyropolus grown crystals produced in Laskar's laboratory [5] were used in the experimental program.

b) Thermal Decomposition Studies (with A. de Panafieu, T. Russell, H. Chaya and A. Mandelis)

Thermal decomposition studies were carried out with the single crystal or powder samples in a Vac-ion pumped ultra high vacuum system capable of a base pressure of 10^{-9} torr. The total pressure in the system was measured with an ionization gauge in the sample chamber and a U.T.I. mass spectrometer was used to measure the partial pressure of various species. Because of low sensitivity at the potassium mass number and interference due to hydro-carbon molecules, a potassium flux meter [6,7] was developed and used in later decomposition studies. The decomposition rate was determined by measuring the change of pressure in the sample chamber under continuous pumping conditions. The decomposition rate is then given by: $R(t,T) = (KS)(\Delta p/A)$ molecules cm^{-2} sec^{-1}, where $K = 3.27 \times 10^{19}$ molecules l^{-1} $torr^{-1}$. A is the Area of the sample in cm^2, Δp is the change in pressure in torr and S is the pump speed in liter/sec^{-1}.

Measurement of $\Delta p(T)$ was made either at constant temperature or with the temperature being varied at a constant rate. Good agreement was obtained between these two methods indicating that thermal gradients were not significant in the constant heating rate experiments in which $(dT/dt) \simeq 0.5$ K.s^{-1}. Typical data $\Delta p(N_2)$ as a function of temperature is shown in Fig. 1, which is taken from the paper of de Panafieu et al [8].
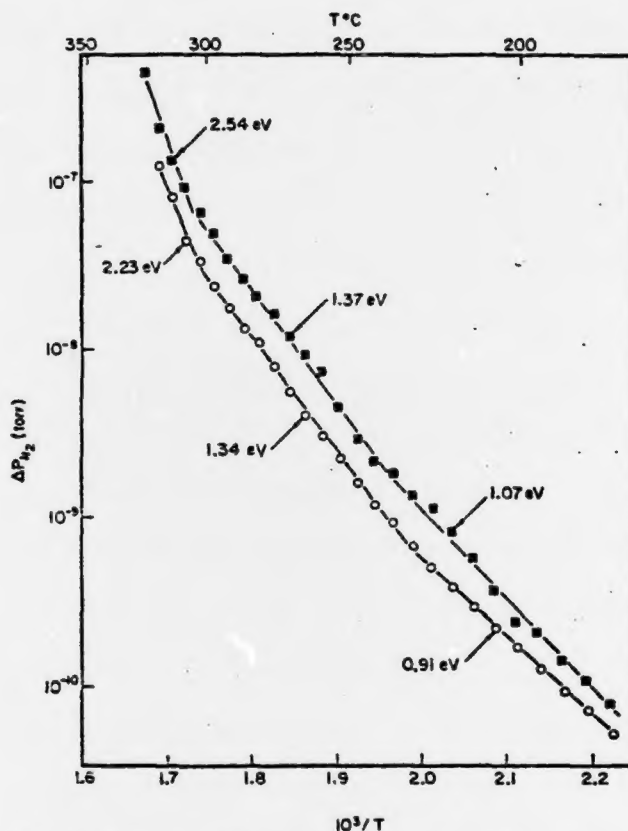

FIG. 1. Temperature dependence of the N_2 partial pressure for a powder sample of KN_3. o, run #5; ■, run #12.

It is seen that more than one activation energy is associated with the decomposition process and that the decomposition rate and the energies of activation were run dependent. The intermediate activation energy of circa 1.35 ± 0.05 eV was the least run dependent.

The presence of three activation energies associated with the evolution of nitrogen over the range of temperatures examined indicates that different processes are rate controlling in these temperature zones. The activation energy of 2.4 ± 0.2 eV observed in the high temperature region is in reasonable agreement with the value of 2.13 eV determined by Jacobs and Thompkins in the same temperature range. If, as Jacobs and Tompkins suggested, the activation energy in the high temperature range is associated with the thermal excitation of an azide ion, other processes must be rate controlling in the lower temperature regions. The correspondence between the measured activation energies for nitrogen evolution and the energies associated with charge transport in KN_3 by potassium vacancy migration [8] may indicate that bulk ionic charge transport is involved in these low temperature regions. There is, however, a discrepancy between the "break points" of the activation energy regions in the ionic conductivity and the gas evolution data that would seem to be outside the joint experimental error. A similar correspondence between activation energies for conductivity and de-composition has been reported for NaN_3 by Tokar et al.[10]

Data was harder to obtain on the potassium partial pressure but this also indicated a change in the temperature dependence of this parameter at about 300°C. Only two regions could be found due to signal to noise problems resulting from the potassium partial pressure being approximately three orders of magnitude lower than that for N_2.

Although the high temperature decomposition data is in reasonable agreement with previous measurements obtained using closed systems rather than continuous pumping, the behavior at low temperatures has not previously been observed. It is known that the presence of gaseous ambients do influence thermal decomposition behavior. In an attempt to determine if

the difference between the closed and open system experiments resulted from the presence of the decomposition products in the former, some studies were made in the dynamic vacuum system with the sample contained in a Knudsen cell. In this configuration the sample is in contact with its decomposition products and the effusion rate from the cell depends directly upon the decomposition rate. The partial pressure change in the dynamic vacuum system resulting from this effusion can be measured as before and used to monitor the decomposition kinetics. The data obtained monitoring the nitrogen evolution was found to be of the same form as that shown in Fig. 1 above, the lower activation energy regions found at low temperatures still being present and the tendency towards higher decomposition rates and reduced activation energies as a function of the number of runs still being observed. Potassium evolution from the Knudsen cell was monitored using the fluxmeter. With a fresh single crystal specimen very little potassium evolution was observed if the cell temperature was not allowed to go above circa $308 \pm 6°C$. If the sample wa; heated above this temperature, however, the potassium flux was found to increase by about two orders of magnitude. After this behavior appreciable potassium evolution was observed at temperatures below the threshold temperature and the nitrogen evolution rate was also found to have increased by about two orders of magnitude. Removal of the top from the Knudsen cell allowed more potassium to escape in a given time and the threshold for the onset of enhanced decomposition was detectable about 5° lower in temperature than before. However, with the potassium allowed to escape from the cell the decomposition rate above this threshold temperature was found to be only about 25% of that obtained when the potassium was in pseudo-equilibrium with the crystal surface. The nitrogen evolution was also lower than found in the capped

cell experiments by about a factor of four. This data is in general
agreement with earlier measurements of Jacobs and Tomkins [9] where the
presence of alkali metal was found to enhance the decomposition rate of
KN_3. It indicates that considerable care must be taken in interpreting and
comparing absolute decomposition rates determined under different experi-
mental conditions.

Measurements are currently in progress to determine the effect
of a controlled nitrogen ambient on the decomposition behavior. The
potassium evolution is monitored since the N_2 background pressure masks
the nitrogen evolution during decomposition. The preliminary data indi-
cates that potassium evolution is reduced by the presence of the nitrogen
ambient. Experiments are in progress to determine if this is due to reduced
decomposition of the sample. If this is found to be the case additional
gaseous ambients that can couple to the vibrational states of the N_3^- ion
will be investigated as possible decomposition inhibitors.

c) The Effects of Electric Fields on the Thermal Decomposition
    (with A. de Panafieu and H. Chaya)

In order to evaluate the role played by the transport of
charge species in the bulk of the crystal during thermal decomposition
and to evaluate the possible role of N_3^- lifetime on the decomposition
reaction in an azide having Schottky rather than Frenkel lattice dis-
order, a series of experiments were performed in which a constant electric
field was applied to a crystal decomposing at a given temperature. The
resulting changes in the decomposition rate and the ionic conductivity
were measured as a function of time. Upon application of the field, the
ionic current made a step increase with a response time determined by
the associated measuring electronics and then decayed as a function of
time to a temperature dependent steady state value. During this period
the equilibrium pressure in the decomposition chamber increased slowly

with a relaxation time that was essentially the same as that for the
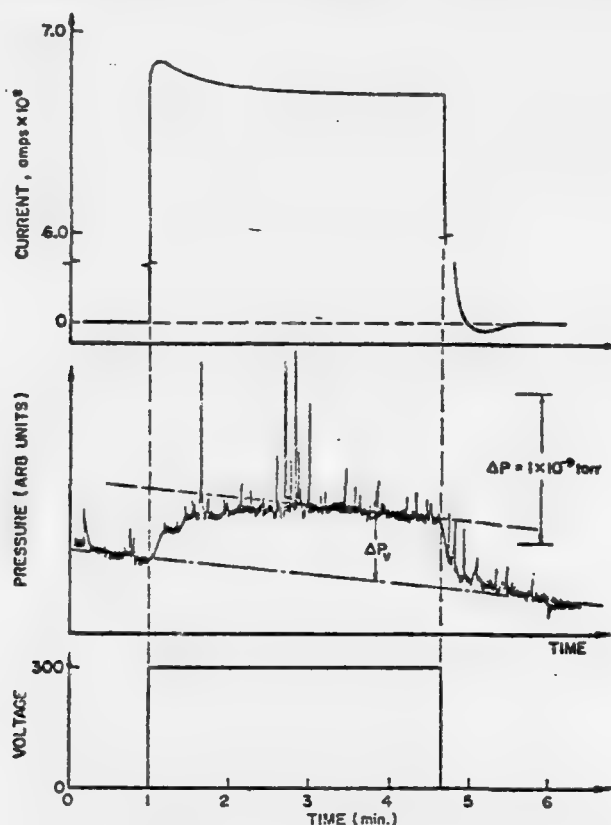current decay. Typical data [8] is shown in Fig. 2 which clearly

FIG. 2 Time dependence of the ionic current and the asso-
ciated change in pressure for a KN_3 single crystal upon the
application of a dc bias.

indicates that no sudden increase of pressure was observed upon the
application of the field. Due to the limitations of apparatus sensitiv-
ity, these measurements were only possible over the restricted temperature
region between 500 and 540 K, an ionic current on the order of 10^{-7} A
being associated with a change in nitrogen partial pressure of ca. 10^{-9} torr.
This pressure change had to be measured with the ionization gauge since
the mass spectrograph induced a current of about 10^{-6} A in the electrometer
circuit. Mass spectrographic analysis of the field enhance decomposition
products was made in separate runs and indicated that once again, N_2 gas was
being evolved. The changes in the K partial pressure were too low to be de-
tectable using the mass spectrometer during this experiment.

Later experiments with a revised electrode configuration and with the potassium flux meter in the vacuum system enabled measurements to be made over a wider temperature range and the potassium evolution to be followed. This series of measurements indicated the same general behavior for the nitrogen evolution as that discussed above. However, the evolution rate was found to be sensitive to the prior electric field history of the decomposing sample. In general, the field enhanced decomposition rate took longer to reach its saturation value when the sign of the field was reversed from that of the previous run. This behavior is consistent with the need to establish a polarization field in the sample before decomposition is enhanced or to reach a certain ad-atom coverage of the decomposing surface due to bulk transport processes.

Measurements were made of both the nitrogen and potassium evolution with an electrode configuration that was designed to permit decomposition products to escape from only one of the large area crystal faces. Nitrogen evolution was found to be enhanced for both signs of the applied field with the enhancement being the same to within a factor of two. The evolution of potassium was asymmetric with applied field direction being greatest when the front surface had a negative polarity i.e. when the number of potassium ad-atoms on that surface had been increased by bulk transport processes. The voltage dependence of the enhanced potassium flux is shown in Fig. 3. A power law fit to the data for negative polarity indicates a dependence of the potassium evolution rate on applied voltage varying as the 1.7th power.

When an insulator was inserted between the sample and the grid electrode so that no steady state current could flow, no field enhanced decomposition was observed. With a non-blocking electrode configuration the ratio of the additional number of nitrogen molecules leaving the
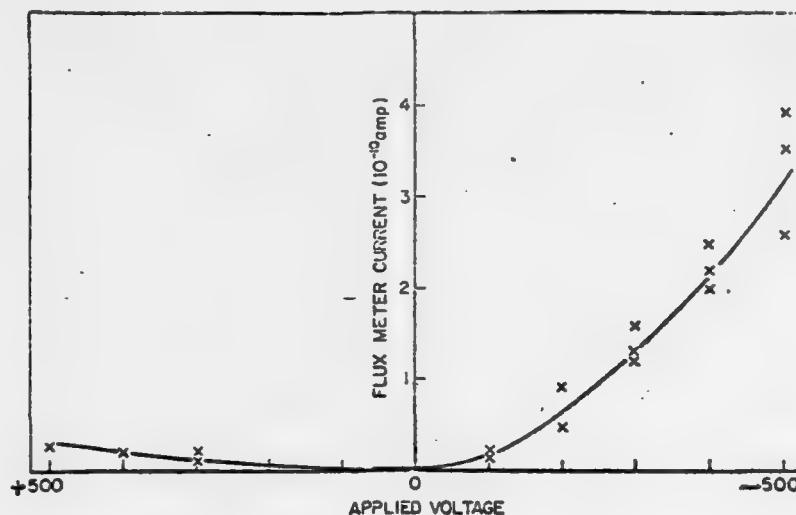
Fig.3. Dependence of Potassium Flux on the sign of
the applied voltage during thermal decomposition.

surface due to the applied field,to the bulk charge flow was on the order

of unity over a wide temperature range. This fact together with the

observed asymmetry of the potassium evolution suggests that the field

contribution to decomposition arises from a solid state electrolytic

behavior. If this is correct then the rather symmetric enhancement of

the nitrogen evolution rate for both signs of applied field may be due

to the following processes. With the decomposing surface negative,

positive ion vacancies are moved away from this region and the surface

obtains an excess of potassium ad-atoms. It has been indicated by the

measurements of both Garner and Marke [11] and Jacobs and Tompkins [9]

that excess potassium on the surface increases the decomposition rate.

The enhanced evolution of nitrogen gas observed in the present measurements

under negative voltage conditions would therefore be due to this excess

potassium, which would be maintained at the surface in concentrations

dependent upon the bulk ionic current and the potassium evaporation

kinetics. For the decomposing surface positive, the flux of potassium

ion vacancies is towards the decomposing surface. This flux has the effect of creating an excess concentration of azide ad-atoms on the surface which must be responsible for the increased decomposition rate under this sign of the field. In this case, the high field at the surface may assist in removing the electron from the azide ion to the electrodes. This would be consistent with the observation that decomposition in the presence of the field occurs preferentially at those regions of the surface under the electrode grid where the field is highest.

Theoretical   (with A. Danemar and D. O. Welch)

a) The azide repulsive potential and Schottky formation and migration energies

The alkali azides represent an ionic system that is more complicated to treat theoretically than the alkali halides due to the non-spherical shape of the Azide ion. The Born approach [19] to the evaluation of the cohesive energy and energies of defect formation and migration etc., can however be applied if such a potential is developed. Initial calculations by Gray and Waddington [13] treated the azide ion as an ellipsoid of revolution as far as its repulsive interaction was concerned. This is not a good approximation to the electron density distribution on the azide ion and in an attempt to obtain a repulsive potential that better fitted this distribution and which could be applied to a series of alkali azides, a double spherical potential was developed [14]. This potential was used in calculations of the energies of Schottky pair formation and cation migration in potassium azide. For comparison purposes the calculations were also performed using the original Gray and Waddington repulsive potential and a modified version of this potential designed to provide a better fit to the equilibrium unit cell volume and elastic properties

of KN_3. In calculating the lattice properties Coulambic, repulsive, van der Waals and polarization energy contributions were taken into account.

The potential energies required to form K^+ and N_3^- vacancies and K^+ saddle point configurations for motion along the <110> and <001> directions were also calculated. The calculation involved treating the defect formation energy in a rigid crystal with unpolarized ions and then adding contributions to the total formation energy arising from ionic relaxation and crystal polarization. Only nearest neighbor positional relaxations were taken into account. For the azide ions these relaxations involve angular displacements as well as the motion of the center of mass. Again these calculations were performed using the three forms of the azide repulsive potential. Tables 1 and 2 summarize the results of these calculations.

b) Cation Diffusion in Potassium Azide

The diffusion of potassium tracers in KN_3 has been measured by Sharma and Laskar [15]. The above theoretical calculation indicated that there is a significant anisotropy in the cation vacancy migration energy in KN_3 with the <001> direction having the lowest energy for both the modified Gray and Waddington and the Dispherical forms of the azide repulsive interaction. In order to provide more insight into the diffusion data a calculation [16] was performed of the temperature dependence and anisotropy of the tracer self diffusion coefficient of potassium ions in KN_3. A vacancy mechanism was assumed to be operative. The calculation was performed in the spirit of a treatment of isotropic materials due to Mullen [17] but with the anisotropy of KN_3 taken into account. For motion along the c-axis the cation sites form a one-dimensional chain and for a

vacancy mechanism the correlation factor is zero. Matter transport along this direction must therefore involve vacancy jumps in the basal planes of the tetragonal KN_3 structure and motion along the <110> directions will therefore play a dominant role in determining the diffusion rate for tracers parallel to the c-axis.

c) Born Model Calculations of the Properties of the Alkali Azides

The success of the above calculations in describing the behavior of KN_3 indicated the desirability of extending the Born approach to other members of the family of the alkali azides but using the potentials developed for the azide ion in the KN_3 calculations. Such calculations were performed [18] to obtain the cohesive energies, lattice parameters and specific volumes of NaN_3, RbN_3 and CsN_3 as well as KN_3. Lattice stability to small deformations was also investigated. NaN_3 has a rhombohedral structure and it was found that only the Double Spherical forms of the azide repulsive interaction gave good agreement for this azide lattice as well as for the tetragonal structures possessed by the other members of the family. Since properties depending upon the second derivative of the potential are a more sensitive test of its validity, calculations were also made [19] of the azide librational frequencies and the elastic moduli for NaN_3, KN_3, RbN_3 and CsN_3, using the same modified Born model discussed above. These calculations also favor the dispherical form of the azide repulsive potential over the elipsoidal form, either in its original Gray and Waddington formulation or with a modified stiffness parameter.

energy (eV)	K⁺ vacancy			N₃⁻ vacancy		
	GW I	GW II	DS	GW I	GW II	DS
E_f^a Coulombic		4.02			3.45	
van der Waals		0.12			0.28	
repulsive	−0.45	−0.40	−0.49	−0.54	−0.48	−0.49
total	3.69	3.74	3.65	3.19	3.25	3.24
E_{pol}^0		−2.41			−2.14	
E_{rel}	−1.13	−1.06	−0.65	−0.36	−0.30	−0.31
total relaxation energy	−3.54	−3.47	−3.06	−2.50	−2.44	−2.45
formation energy	0.15	0.27	0.59	0.70	0.82	0.80
Schottky pair	0.85	1.09	1.39			

Table 1. Components of the energy of Schottky pair formation

energy (eV)	⟨110⟩			⟨001⟩		
	saddle point formation					
	GW I	GW II	DS	GW I	GW II	DS
E_f^a Coulombic		2.18			2.28	
van der Waals		−0.15			0.07	
repulsive	2.35	3.85	3.92	0.73	1.28	1.70
total	4.38	5.88	5.95	3.08	3.63	4.05
E_{pol}^0		1.69			1.52	
E_{rel}	−2.36	−3.20	−2.23	−1.20	−1.33	−1.01
total relaxation energy	−4.05	−4.89	−3.92	−2.72	−2.85	−2.53
formation energy	0.33	0.99	2.03	0.36	0.78	1.52
	vacancy migration					
E_f^0	0.69	2.14	2.30	−0.61	−0.11	−0.40
$\Delta(E_{pol}^0 - E_{rel})$	−0.51	−1.42	−0.86	−0.82	−0.62	−0.53
migration energy	0.18	0.72	1.44	0.21	0.51	0.93

Table 2. Components of the energies of cation saddle
point formation and vacancy migration

REFERENCES

1. D. A. Young, Progress in Solid State Chemistry $\underline{5}$, (1970) 401.

2. G. G. Savel'ev, Yu. A. Zakharov and V. B. Spitsa. Russ. J. Phys. Chem. $\underline{39}$ (1965) 1500.

3. M. P. Tosi. Solid State Physics $\underline{16}$ (1964) 1.

4. J. N. Appleton and J. Sharma. Mat. Res. Bull. $\underline{5}$ (1970) 227.

5. D. L. Foster, K. A. Wagner and A. L. Laskar. J. Crystal Growth $\underline{32}$ (1976) 33.

6. H. V. Thapliyal, E. K. Stafanakos and R. F. Tinder. Surface Science 38 (1973) 231.

7. S. Tomada, K. Kodera and I. Kusunoki. Surface Science $\underline{45}$ (1974) 657.

8. A. de Panafieu, B. S. H. Royce and T. Russell. J. Chem. Phys. $\underline{64}$ (1976) 1473.

9. P.W.M. Jacobs and F. C. Tompkins. Proc. Roy. Soc. (Lond.) Series A $\underline{215}$ (1952) 265.

10. K. Tokar, H. T. Spath and G. W. Herzog. Reactivity of Solids. Wiley, New York (1969) p. 287.

11. W. E. Garner and D. J. B. Macke. J. Chem. Soc. (1936) 657.

12. M. P. Tosi. Solid Sate Phys. $\underline{16}$ (1964) 1.

13. P. Gray and T. C. Waddington. Proc. Roy. Soc. 235A (1956) 481.

14. A. Danemar, D. O. Welch and B. S. H. Royce. Physical Status Solidi (b) $\underline{55}$ (1973) 201.

15. J. Sharma and A. L. Laskar. J. Phys. Chem. Solids $\underline{34}$ (1973) 909.

16. A. G. Danemar, B.S.H. Royce and D. O. Welch. Phys. Status Solidi (b) $\underline{65}$ (1974) 153.

17. J. G. Mullen. Phys. Rev. $\underline{124}$ (1961) 1723.

18. A. Danemar, B.S.H. Royce and D. O. Welch. Phys. Status Solidi (b) 70(1975) 663.

19. D. O. Welch, A. Danemar and B.S.H. Royce. Physica Status Solidi (b) $\underline{71}$ (1975) 159.